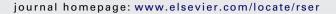


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Biodiesel feasibility study: An evaluation of material compatibility; performance; emission and engine durability

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ABSTRACT

Biodiesel, derived from the transesterification of vegetable oils or animal fats, is composed of saturated and unsaturated long-chain fatty acid alkyl esters. In spite of having some application problems, recently it is being considered as one of the most promising alternative fuels in internal combustion engine. From scientific literatures, this paper has collected and analyzed the data on both advantages and disadvantages of biodiesel over conventional diesel. Since the aim of this study is to evaluate the biodiesel feasibility in automobiles, the first section is dedicated to materials compatibility in biodiesel as compared to that in diesel. The highest consensus is related to enhanced corrosion of automotive parts due to its compositional differences. In the subsequent sections, data on performance, emission and engine durability have been analyzed and compared. In this case, the highest consensus is found in reducing emissions as well as in increasing moving parts sticking, injector coking and filter plugging. This paper has also summarized the factors of biodiesel in contributing these technical performances.

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1. Introduction

Recently, world has been confronted with an energy crisis due to fossil fuel depletion and environmental degradation. Biodiesel is one of the most promising alternative fuels to meet these problems. It is renewable, biodegradable, non toxic and has almost very close property to that of diesel fuel [1–5]. It can be produced form vegetable oil as well as animal fats. Oils/fats are basically triglycerides which are composed of three long-chain fatty acids [6–8]. These oils/triglycerides have higher viscosity and

is therefore cannot be used as fuel. In order to reduce viscosity, triglycerides are converted into esters by transesterification reaction. By this means, three smaller molecules of ester and one molecule of glycerin are obtained from one molecule of fat/oil. Glycerin is removed as by product and esters are known as biodiesel.

Just like petroleum diesel, biodiesel operates in compressionignition engines with little or no modification [9]. Moreover, biodiesel offers advantages regarding the engine wear, cost, and availability [10,11]. When burned, biodiesel produces pollutants that are less detrimental to human health [12,13]. In addition, it provides better lubricity as compared to that of diesel fuel [14]. But, due to its unsaturated molecules and compositional effects, it is more oxidative and causes enhanced corrosion and material

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Table 1Wear data from laboratory wear test: wear in biodiesel as compared to diesel.

Ref.	Biodiesel	Method	Results
Wain [51]	B20 (Soybean)	Four ball test	L
Mansjuki and Maleque [52]	B5	Pin-on-disc	L
Kalam and Masjuki [53]	B20 (Palm oil)	Four ball wear	L
Dalai et al. [54]	B1 (Canola oil)	Roller on cylinder	L
Goodrum and Geller [55]	B (0.1-5) [rapeseed, soybean, castor]	HFRR	L
Rashid et al. [56]	B100 (Moringa oleifera oil)	HFRR	L

L = less wear, S = similar wear, H = higher wear.

degradation [15-17]. Geller et al. [18] found that copper alloys were more prone to corrode in biodiesel as compared with ferrous alloys. Haseeb et al. [19] observed that biodiesel is not only corrosive but also causes degradation of its fuel properties. Kaul et al. [20] found that biodiesels from Jatropha curcas and Salvadora were more aggressive for metals than biodiesels from Karanja and Mahua. Kaul et al. [20] observed that copper alloys were more prone to corrosion in biodiesel as compared with ferrous alloys. Corrosion attack was also reported even for lower biodiesel (2%) blend levels [16]. Biodiesel upon exposure of different metals not only shows its aggressive corrosiveness but also undergoes degradation in fuel properties [16.18.21.22]. Increased polarity and solvency property have also been reported to degrade elastomer materials [23-25]. However, it is noted that the factors in contributing degradation of automotive materials and fuel properties include presence of oxygen moieties, free fatty acids, degree of unsaturation, hygroscopic nature etc. These factors are also found to influence the performance, emission and engine durability while biodiesel is used as a fuel partially or completely.

However, performance and emission characteristics of biodiesel-fueled engine are something crucial. Combustion of biodiesel fuel in compression-ignition (CI) engines in general results in lower smoke, particulate matter, carbon monoxide and hydrocarbon emissions compared to diesel combustion while the engine efficiency is either unaffected or improved [26–28]. However, these are influenced by a number of factors including lower heating value [29], increased viscosity [30], higher density [31], less calorific value [32], oxygen content [33], auto-oxidation [34] of biodiesel etc. In order to minimize the adverse effect of these factors, many researchers added different blending components such methanol to improve viscosity [35], ethanol to reduce fuel consumption [28], additives to reduce oxidation [34] etc. This is in general agreement that using biodiesel in diesel engines can reduce HC, CO and PM emissions but NO_x emission may increase [36,37]. The increase in NO_x emission has been tried to reduce by adapting many ways such as through modifying the properties of the biodiesel [38], by adjusting engine setting [39] by emulsified water [40], emulsified methanol and ethanol [41,42] etc. However, most of these methods also lead to deterioration in engine performance as well as degradation of automotive components.

In some cases, use of biodiesel in internal combustion engine may lead to engine durability problems including injector cocking, filter plugging and piston ring sticking, severe engine deposits etc. [43–45]. In order to assess the durability of different engine components, many researchers conducted their studies by static engine tests as well as field trials. National Biodiesel Board (NBB) [46,47] has reported that in 1000 h durability test of engine with B20 (Soyester blend) caused some technical problems like failure of engine pump, softening of fuel system seals, deposits on air box covers, piston components and injectors. Kenneth et al. [48] and Kearney et al. [49] conducted different field trail tests by using B20 and they found no unusual engine wear as compared to that in diesel fuel. Similar results have also been reported by Chase et al. [50] even for B50 biodiesel blends in long term field trail test. However filter plugging, injector cocking were the common problems

in most of the studies. The aim of this study is to characterize the function of different factors of biodiesel and thereby to evaluate its feasibility in automobile application.

2. Material compatibility

2.1. Wear

Depending on applications where sliding contacts are involved, wear and friction are occurred. The common sliding components in automobile engine are cylinder liner, bearing, cam, tappet, crankshaft journals, pistons and piston pins, valve guides, valve systems etc. Lubricity of these components is normally provided by the fuel itself. Biodiesel inherently provides better lubricity than diesel fuel [21]. However, wear and friction may increase if the fuel is hygroscopic in nature. Biodiesel is such type of fuel, which can absorb moisture and thereby can increase corrosive wear. In addition, auto-oxidation of biodiesel is most likely prone to influence wear characteristics. To understand the comparative wear in diesel and biodiesel, several laboratory investigations with four ball wear machine, pin-on-disk wear testing machine, reciprocating wear tester etc. have been performed by some researchers. All these laboratory tests basically have been conducted in order to simulate the wear in engine parts that are in contact with biodiesel. The laboratory wear test data for biodiesel as compared to that in diesel fuel has been summarized in Table 1.

Masjuki and Maleque [52] have investigated the anti-wear characteristics of palm oil methyl ester (0%, 3%, 5%, 7%, 10%) in lubricant. They observed that 5% POME can provide better lubricity. Lubricant containing more than 5% POME causes higher wears damage due to oxidation and corrosion. According to Knothe and Steidley [57], Holser and Harry-O'Kuru [58] biodiesel always provides better lubricity than that of diesel fuel. Trace components found in biodiesel fuels including free fatty acids, monoglycerides, diglycerides are reported to improve the lubricity of biodiesel [59]. Oxygen containing compounds such as free fatty acids, esters are superior wear and friction reducing agents [21]. These compounds adsorb or react on rubbing surfaces to reduce adhesion between contacting asperities and thereby limit friction, wear and seizure.

Like laboratory wear tests, many studies have also been done by static engine or field trail tests (Tables 2 and 3). In addition to inspection of the wear affected components, some studies have analyzed oil and ash to find out the sources of wear materials and their amounts. It is seen from Table 4 that wear in biodiesel is almost similar or less with relative to that in diesel. In fact, due to having higher lubricity property in biodiesel, it causes overall reduced wear. But some metals like copper, zinc, and aluminum have been found in higher percentage and are therefore considered as incompatible with biodiesel. Clark et al. [60] have investigated wear in diesel fuel, methyl and ethyl soyate (with and without additives) by oil analysis and by weight, dimensional measurement of parts before and after running engine. The rod and main bearings have been weighed for loss of material and obtained results showed normal wear. They have found no notable differences in wear for individual fuels. But Agarwal [61] have shown 30% less

Table 2Wear result in biodiesel as compared to that in diesel fuel by static engine test.

Ref.	Biodiesel blend	Engine operation	Analysis	Result
Kalam and Masjuki [63]	15% POD	300 h	Oil	L
Agarwal et al. [64]	B20	500 h	Oil	L
Clark et al. [60]	B100 (Methyl and ethyl soyate)	200 h	Oil	S
Peterson et al. [65]	Rapeseed methyl and ethyl ester	200 h	Oil	S

L = less wear, S = similar wear, H = higher wear.

Table 3Wear result in biodiesel as compared to that in diesel fuel in field trail test.

Ref.	Biodiesel blend	Engine operation	Analysis	Result
Fraer et al. [62]	B20	4 yr	Oil	S
Bickel and Strebig [66]	B20	2 yr	Oil	S
Kenneth et al. [48]	B50, B100	200,000 km	Oil	S
Clark et al. [60]	B20	2 yr	Oil	S
Agarwal et al. [67]	B100	30,000 km	Oil	L

L = less wear, S = similar wear, H = higher wear.

wear (by measuring dimensional change) in B20 as compared to diesel fuel. Fraer et al. [62] carried out an investigation by field trial with B20 and diesel fuel for 4 yr. They found almost identical wear in both fuels. However, they noticed that both diesel and B20 engines showed wear in bearing copper liners. Engines of B20 showed scuffing in piston valve and became unsuitable for reuse whereas it was still useable in engine running on diesel.

The maximum test duration for the experiments that have been listed in Table 1 is around 1 h while in Table 2 is around 500 h. On the other hand, most of the field trail tests in Table 3 are of 2–4 yr. Based on the obtained results as stated in Table 1, it can be said that that during short term test (1 h), biodiesel provides better lubricity than diesel. On the other hand, during long term test, biodiesel loses its lubricity as evidenced by the results in Table 3. In long term test, auto-oxidation as well as corrosiveness of biodiesel seems to play an important role in material degradation.

Peterson et al. [65] conducted 200 h static engine tests with four-stroke engines. The used fuels were diesel, neat rapeseed methyl and ethylesters, neat hydrogenated soybean-oil ethylester (frying oil ethylester), as well as B20 blends of the hydrogenated soy ester with diesel. No significant problems were encountered in these tests. At the conclusion of the test, iron in lube oil was significantly higher for the rapeseed oil based fuels compared to diesel suggesting abnormal wear. This was not the case for the hydrogenated soybean-oil fuels. The unsaturation of the rapeseed ester fatty acid chains probably lead to oxidation and acid formation causing corrosion. But, according to the lab investigation by Knothe and Steidley [57], Holser and Harry-O'Kuru [58] unsaturated molecules provide better lubricity as compared to saturated molecules. So, in practical case, corrosion may play an important role to influence wear in biodiesel.

2.2. Corrosion

Although, the acceptance of biodiesel in automobile applications is relatively a successful story, questions continue to arise with regards to its corrosive nature and degradation of fuel properties. The fuel system in modern diesel engine includes many precision parts which are made from different ferrous or nonferrous alloys. Though these parts are quite corrosion resistant, corrosion damage of fuel system parts is accelerated considerably when the fuel becomes oxidized or absorbs moisture from air. With compared to diesel, biodiesel is more prone to absorb water, causes microorganism contamination and also permits the development of electrochemical corrosion processes [22,68,69]. ASTM D130 is used to measure the level of copper corrosion that would occur if biodiesel are used in any application where metals such as copper are present. This test is accomplished by using a copper strip tarnish test in order to monitor the presence of acids in the fuel. Similarly, TAN value is another parameter measured by titration to indicate the total acid number. In fact, both of these methods are not reliable to understand the corrosiveness of individual organic acids [16.18].

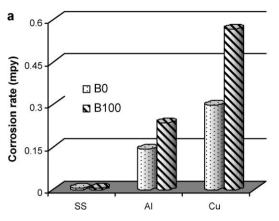
There are number of studies available in the literature related to corrosion of different metals in biodiesel [15,16,18–20,70]. Kaul et al. [20] investigated the corrosiveness of different biodiesel (i.e. *Jatropha curcas*, Karanja, Mahua and salvadora) as compared to that of diesel fuel. They found that biodiesel from *Jatropha curcas* and Salvadora were more corrosive for both ferrous and non-ferrous metal. Geller et al. [18] conducted immersion test in fat based biodiesel for different ferrous and non-ferrous metals. They observed that copper alloys were more prone to corrosion in biodiesel as compared to ferrous alloys. According to Sgroi et al. [15], sintered bronze filters in oil nozzle were subjected to

Table 4Wear element in engine oil for biodiesel as compared to that in diesel.

Ref.	f. Biodiesel blend		Test		Elemental results				
		Static engine	Field trial	Cu	Fe	Cr	Al	Zn	Pb
Jakab et al. [68]	B100 (Palm oil)	200,000		Н	L	L	Н	_	Н
Kenneth et al. [48]	B20 (Soybean)		2 yr	S	S	S	_	_	_
Jianbo et al. [59]	B7.5 (palm oil)	300 h	•	L	L	_	_	Н	L
Fraer et al. [62]	B20 (Soybean)		4 yr	L	L	L	L	L	L
Clark et al. [60]	B100 (MS and ES)a	200 h	•	Н	L	L	Н	_	Н
Agarwal et al. [64]	B20	500 h		L	L	L	-	L	L

H = high wear, S = similar wear, L = less wear.

^a (Methyl and ethyl soyate).



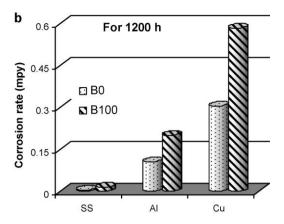
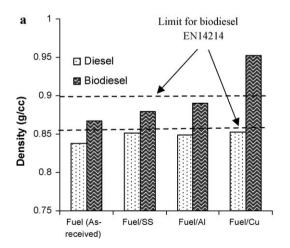


Fig. 1. Corrosion rate of stainless steel, aluminum and copper in diesel and biodiesel after immersion for (a) 600 h and (b) 1200 h at 80 °C [71].

pitting corrosion in biodiesel at 70 °C after 10 h of operation. Corrosion attack for turne sheet metal was also reported even for lower biodiesel (2%) blend levels [16] while diesel shows no corrosiveness. Fazal et al. [71] investigated the corrosion behaviour of different automotive materials in palm biodiesel. They observed that copper and aluminium were subjected to corrosion while stainless steel was not (Fig. 1). Fuel properties such as density and viscosity were also changed a lot due to the metal contact (Fig. 2). Thus, biodiesel upon exposure of different metals not only shows its aggressive corrosiveness but also undergoes degradation in fuel properties [16,19,21,22].

Concerns arise from the fact that biodiesel is more hygroscopic in nature as compared to diesel [72], has higher electrical conductivity [23] and increased polarity and solvency [23,24]. Free water in biodiesel is undesirable because it may promote microbial growth and corrodes fuel system components [24,73]. Due to having solvency property it can deface the metal protecting paints/coatings and thereby bring the metal in contact with biodiesel for further reaction. Increased polarity and solvency also cause degradation of elastomer materials [25]. In addition, auto-oxidation of biodiesel can reconvert esters into different mono-carboxylic acids such as formic acid, acetic acid, propionic acid, caproic acid etc., which are responsible for enhanced corrosion and degradation of fuel properties [26]. The presence of high levels of unsaturated fatty acid methyl esters (FAME) makes biodiesel very susceptible to oxidation as compared to petroleum diesel [74]. According to Sarin et al. [75] during oxidation process, the fatty acid methyl ester usually forms a radical next to double bond and then quickly bond with the oxygen from air. This process may change the fuel properties including viscosity, total acid number, density, iodine value, pour point, cloud point etc. Increased acidity and peroxide value as a result of oxidation reactions can also cause the corrosion of fuel system components, hardening of rubber components and fusion of moving components [76,77].

Studies on the fundamentals of corrosion inhibition of metals in biodiesel are scarce. Mitigation of corrosion damage in oil, diesel or different acid solutions using different types of corrosion inhibitors has long been investigated. Imidazolines, primary amines, diamines, amino-amines, oxyalkylated amines, naphthaneic acid, phosphate esters, dodecyl benzene sulfonic acids are the common corrosion inhibitors used in oil and gas [78]. According to Raiasekar et al. [79], corrosion inhibition efficiencies of dodecyl carboxylic acid-based and amine-based carboxylic acid compounds in diesel for API 5LX steel are 90-93% and 56-88%, respectively. The order of efficient corrosion inhibitor for carbon steel in 20% formic acid and 20% acetic acid solution is isobutymethyltetrahydo-azathione (IBMTAT)>cyclohexyl-tetrahydro-azathione (CHTAT)>cyclopentyl-tetrahydro-azathione (CPTAT) [80]. Isoxazolidine derivatives [21], pyridoxal hydrochloric and pyridoxol hydrochloride [81] etc. for iron and steel; benzimidazole-2-tione, benzoxazole-2-tione [82] for aluminum have been found to be very efficient corrosion inhibitors in acidic media. However, there is very little information available on the use of inhibitor to control corrosion in biodiesel. Hancsok et al. [83] reported that 20 ppm concentration of SID [succinimid derivative (SID) from polyisobutylene (PIB), maleic anhydric and rapeseed methyl ester (RME)] showed excellent corrosion inhibiting property in B0, B5 (5% biodiesel in diesel) and B100. According to Kalam and Masjuki [63], irganor NPA



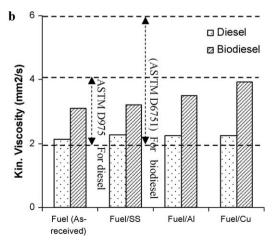


Fig. 2. Changes in (a) density and (b) viscosity for both diesel and palm biodiesel before and after exposure to different metals at 80 °C for 1200 h [71].

can reduce corrosion of metal in palm biodiesel. In conclusion, it is found that although the corrosion characteristics of biodiesel for automotive components have been closely examined, the mechanism and inhibition of corrosion for different materials have hardly been examined in details.

3. Engine performance

Engine performance with biodiesel or its blends depends largely on the combustion, air turbulence, air–fuel mixture quality, injector pressure, actual start of combustion and many other singularities that make test results vary from one engine to another. In addition, it can vary depending on the quality and origin of biodiesel as well as engine operating parameters like speed, load etc. Most of the studies that are available in literature have evaluated the performance of biodiesel-fuelled engine by determining engine power/torque, brake thermal efficiency, brake-specific fuel consumption or energy consumption.

Gumus [84] compared the performance of four-cylinder turbocharged DI engine for diesel and biodiesel/its blends. Results showed that brake-specific fuel consumption (BSFC) of biodiesel (367.68 g/kWh) was higher than that of diesel (299.89 g/kWh). On the other hand, brake thermal efficiency (BTE) of biodiesel (26.30%) was found to be lowered as compared to that in diesel (27.82%). Lin et al. [85] observed 0.371%, 0.667%, 0.889%, 1.30%, 2.37% and 2.85% increase in brake-specific fuel consumption (BSFC) for B5, B10, B15, B20, B25 and B30 (palm biodiesel), respectively, compared with B0. Ramadhas et al. [86] found decreased brake thermal efficiency and increased BSFC (>14%) when rubber seed biodiesel was used against petroleum diesel. Similar results were also reported by Nabi et al. [26], Benjumea et al. [87], Raheman and Ghadge [31], and Ramadhas et al. [88] [Table 5]. Increasing concentration of biodiesel (derived from used cooking oil) in blends decreases engine power and brake thermal efficiency [33]. Slightly different behaviour was found by Raheman and Phadatare [89], where it was reported the maximum thermal efficiency with blends B20 and B40 whilst B100 recorded a poorer performance. This is in agreement with Agarwal and Das [90], who reported that B20 was found to be the optimum biodiesel blend giving maximum increase in thermal efficiency, lowest brake-specific energy consumption (BSEC) and advantage in terms of lower emissions.

This is not surprising that many studies also have reported increased power and torque when using biodiesel. Altiparmak et al. [91] tested different blends of tall oil methyl ester and diesel in a single cylinder direct injection diesel engine at full load condition. They observed that the engine torque and power output with tall oil methyl ester-diesel fuel blends (B50, B60 and B70) increased up to 6.1% and 5.9%, respectively. Similarly, Usta [92] observed an increase in torque and power when using biodiesel from tobacco seed oil in different blends with diesel fuel in four cylinder, four stroke turbocharged indirect injection diesel engine. According to Pal et al. [93], 30% biodiesel blend of thumba oil shows relatively higher brake power, brake thermal efficiency, reduced BSFC and smoke opacity as compared to diesel. Hasimoglu et al. [30] observed that though engine torque decreases from 0.9% to 4.4% at medium and high engine speeds (1800-2800 rpm), it increases from 1.5% to 2.6% at low engine speeds (1100-1600 rpm). They also added that similar trend was also observed for changing in engine power with respect to speed while both BSFC and BTE were increased by 13% and 3%, respectively. These contradictory results may be attributed to fuel properties like density, viscosity; composition, origin of biodiesel as well as the test condition. However, it is difficult to determine the effect of any single fuel characteristics alone on engine performance since many of the characteristics are interrelated [94].

erformance of biodiesel fuel engine as compared to diesel fuelled engine.

Ref.	Engine	Fuel type	Test condition	Increased (vs. diesel)	Decreased (vs. diesel)
Gumus [84]	4C, DI, NA, AC	B0, B5, B20, B50, B100 (Hazelnut kernel oil)	Constant speed: 2200 rpm	BSFC	BTE
Benjumea et al. [87]	TC, DI	B0, B100 (Palm oil)	2000 rpm and 100 Nm	BSFC	BTE
Nabi et al. [26]	1C, NA, DI	B0, B10, B20, B30 (Cottonseed oil)	Constant speed: 850 rpm	BSFC	BTE
Lin and Li [95]	4C, DI	B0, B100 (Fish oil)	800-2000 rpm	BSFC	1
Pal et al. [93]	4C, DI	B0, B100 (Thumba oil)	1000-6000 rpm	Power, BTE	BSFC
Hasimoglu et al.	4C, TC, DI	B0, B100	Speed 1100–1600 rpm	Power, torque, BSFC, BTE	1
30]		(Sunflower oil)	Speed 1800–2800 rpm	BSFC, BTE	Engine power and torque
Ramadhas et al. [86]	1C, DI, NA	B0, B100 (Rubber seed oil)	Speed 1500 rpm	BSFC	BTE
Raheman and Ghadge [31]	Ricardo E6 engine, 1C	B0, B20, B40, B60, B80, B100 (Mahua oil)	Constant 1500 rpm	BSFC	BTE
Utlu and Kocak [96]	4C, DI	B0, B100 (Waste frying oil)	1750-4400 rpm	BSFC	Power, torque
Murillo et al. [33]	3C, DI, NA	B0, B10, B30, B50, B100 (Cooking oil)	950-3450 rpm	BSFC	Power, BTE
Altiparmak et al. [91]	Lombardini 6LD 400, 1C	B0, B50, B60, B70 (Tall oil)	1800-3200 rpm	Power, torque	1
Gogoi and Baruah [97]	1C, 4 stroke	B0, B20, B40, B60 (Kanarja oil)	800-1800 rpm	Power, BTE	1
Qi et al. [27]	1C, NA, DI	B0, B100 (Soybean oil)	1400-2000 rpm	BSFC	Power (less or identical)
Najafi et al. [98]	2C, DI, NA	B0, B10, B20, B30, B40, B50 (Waste cooking oil)	1600-3600 rpm	Power, torque, BSFC	
Aydin and Ilkılıc [28]	1C, DI	B0, B20 (sunflower oil)	1000-3000 rpm	Torque, BSFC	BTE, power
		BO, BE20 (20% ethanol in B100)	1000–3000 rpm	1	Torque BTF: power BSFC (less/similar)

3SFC = brake-specific fuel consumption; BTE = brake thermal efficiency

NC= No. of cylinder; DI= direct injection; IC= intercooled; AC= air-cooled; TC= turbocharged; NA= naturally aspirated

Engine codes:

Performance measuring codes:

Hasimoglu et al. [30] reported that the increments in the engine power and torque at higher speed (1800–2800 rpm) were mainly caused by the higher mixture heating value of the biodiesel. They also added that deterioration of the engine power and torque for biodiesel fuel at low engine speeds (1100-1600 rpm) seemed to cause by the higher viscosity and decreased heating value of boidiesel. Higher thermal efficiency may be related to the atomization of the blends during injection and/or with the stability of the mixtures of fuels during storage, pumping and injection [33]. Increased brake-specific fuel consumption (BSFC) of biodiesel may be attributed to its higher density. It is noted that BSFC is the ratio between mass of fuel consumption and brake effective power [99]. For a certain volume, as it is calculated on weight basis, obviously higher densities of fuel will result in higher values for BSFC [31]. If the density of B100 is 4% higher than that of diesel, which means the same fuel consumption on volume basis will result in 4% higher BSFC in case of B100. The higher densities of biodiesel blends caused higher mass injection for the same volume at the same injection pressure. Slightly different explanation is found by Agarwal [29], who has reported that biodiesel has low heating value, (10% lower than diesel) on weight basis because of presence of substantial amount of oxygen in the fuel. He also added that at the same time biodiesel has a higher specific gravity (0.88) as compared to mineral diesel (0.85) so overall impact is approximately 5% lower energy content per unit volume. The increase of the fuel consumption of biodiesel may also be explained due to its lower calorific value (LCV: 17,150 Btu/lb) compared to that of diesel (18,402 Btu/lb) [32]. In another explanation, the mean increased fractions of brake-specific fuel consumption (BSFC) of different biodiesel blends compared with B0 could be attributed to the gross heating value of palm biodiesel (9760 cal/g) which is about 9% lower than that of premium diesel fuel (10,700 cal/g). As a result, in order to maintain the same brake power output, the BSFC of palm biodiesel blends would be increased to compensate the reduced chemical energy in the fuel [85]. Higher oxygenated nature of biodiesel may also be the reason of its increased BSFC [33]. Based on above discussion, it can be concluded that the influence of biodiesel on engine performance is probably more closely related to several factors including oxygenated nature of biodiesel as well as its higher viscosity and density, lower calorific value etc.

Cheng et al. [35] added 10% methanol in biodiesel in order to improve its performance by modifying the fuel properties. Addition of methanol decreases viscosity and increase in the latent heat of evaporation. The maximum attained brake thermal efficiencies for the diesel, biodiesel (from waste cooking oil), biodiesel with 10% fumigation methanol (air/methanol) and biodiesel with 10% blended methanol obtained by them are 37.2%, 39.1%, 39.6%

and 37.5%, respectively. There are two factors in contributing to the change in brake thermal efficiency upon addition of methanol. Firstly, the methanol will increase the ignition delay, leading to a larger percentage of fuel burned in the premixed mode. This will lead to increase in the brake thermal efficiency. Secondly, the methanol in the fuel will tend to lower the combustion temperature, leading to a decrease in the brake thermal efficiency. In combination of these two factors, though BTE is slightly improved, the BSFC is highly increased. They observed BSFC for ULSD, biodiesel, biodiesel with 10% fumigation methanol and biodiesel with 10% blended methanol are 226.1, 245.6, 254.9, 268 g/kWh, respectively [35]. However, BSFC was successfully reduced whenever 20% ethanol was blended in biodiesel which is defined as BE20. Average brake-specific fuel consumption for usage of BE20 was 20.13% lower than that of B20 [28]. At the same time BTE was found to be higher for BE20 (31.71%) as compared to those of diesel (28.15%) and B20 (25.95%). Similarly, obtained engine torque for BE20 was higher than those obtained for diesel and B20 fuel. Average increase of torque values for BE20 was 1.2% and 1.3% when compared to diesel fuel and B20, respectively.

However, the use of alcohol (methanol/ethanol) has also some limitations, such as lower lubricity, reduced ignitability and cetane number, higher volatility and lower miscibility [100–102] which may lead to increased unburned hydrocarbons emissions [103]. Ethanol, for example, has a cetane rating of 6 and methanol a rating of 35 [104] while for diesel and biodiesel it ranges 40–52 and 48–61, respectively [45]. In addition, direct use of alcohols as fuel may cause corrosion of various parts in the engine [86]. In conclusion it is seen that use of alcohol can improve the performance for biodiesel fuel whenever it is blended with biodiesel. In parallel it is also important to find the effect of methanol/ethanol on material compatibility as well as in engine durability.

4. Emissions

Several numbers of studies have been done to investigate the effect of the biodiesel on exhaust emissions as compared to diesel. Many of these studies [Table 6] have shown that using of biodiesel in diesel engines can reduce hydrocarbon (HC), carbon monoxide (CO) and particulate matter (PM) emissions, but nitrogen oxide (NO_x) emission may increase [26,27,31,43,105]. Few studies have also reported about the decreasing of NO_x [27,28,96,108]. In addition, the percentages of decreased or increased exhaust emission for biodiesel as compared to those in diesel fuel are different for different studies. The reasons explained by different researchers are also different. The heterogeneity in the results and explanation

Table 6Comparative exhaust emissions for biodiesel or its blends relative to petroleum diesel.

Ref.	Fuel type	Increased/Decreased % (vs. Diesel)			
		NO _x	CO	CO ₂	Others
Nabi et al. [26]	B0, B10, B20, B30 (Cottonseed oil)	10% ↑	24% ↓	-	Particulates: 24% ↓
Canakci [106]	B0, B100 (Soybean-oil)	11.2% ↑	18.4% ↓	0.5%↑	Hydrocarbon: 42.5% ↓
McCormick et al. [43]	B0, B20 (Soybean-oil)	0.6% ↑	17.1%↓	_	Hydrocarbons: 11.6% ↓Particulates: 16.4% ↓
Haas et al. [107]	BO, B100 (Soybean-oil)	1.3% ↑	48% ↓	_	Hydrocarbons: 55% ↓ Particulates: 53% ↓
Raheman, and Ghadge [31]	B0, B20, B40, B60, B80, B100 (Mahua oil)	6% ↑	Min 12% ↓ Max 81% ↓	_	Smoke density: 5%
Utlu and Kocak [96]	B0, B100 (Waste frying oil)	1.45% ↓	17.14% ↓	8.05% ↓	=
Murillo et al. [33]	B0, B10, B30, B50, B100 (Cooking oil)	16% ↑	10% ↓	_	=
Altiparmak et al. [91]	B0, B50, B60, B70 (Tall oil)	30% ↑	38.9%↓	_	=
Qi et al. [27]	B0, B100 (Soybean-oil)	5% ↓	27% ↓	_	Hydrocarbon: 27% ↓ Smoke: 52% ↓
Kegl [108]	BO, B100 (Rapeseed oil)	25% ↓	25% ↓	_	Hydrocarbon: 30% ↓ Smoke: 50% ↓
Aydin and Ilkılıc [28]	B0, B20 (sunflower oil)	15% ↓	32.5% ↓	67% ↓	SO ₂ : 44% ↓
	B0, BE20 (20% Ethanol in B100)	12% ↓	16.67% ↓	18.75% ↓	SO ₂ : 52% ↓
Cheng et al. [35]	B0, B100 (waste cooking oil)	4.1% ↑	9.2% ↓	Similar	Hydrocarbon: 36.8% ↓
	B0, BM10 (10% methanol in B100)	6.2%↓	_	2.5% ↓	=
	B0, BM10 (10% fumigated methanol)	8.2% ↓	-	2.5% ↓	-

obtained by different authors can also be attributed to differences in the origin of biodiesel as well as the test condition of engine.

The majority of studies have found sharp reductions in exhaust emissions with biodiesel as compared to diesel fuel. The more accepted reasons in reduction of emissions particularly CO, CO₂, hydrocarbons, SO₂, particulates, smoke can be attributed to presence of sufficient oxygen in biodiesel. As mentioned previously, biodiesel contain 10% oxygen while diesel has no oxygen content [90]. Increased amount of oxygen in fuel-rich combustion zone is believed to ensure more complete combustion and thereby reduces exhaust emissions [33]. Complete combustion can convert CO into CO₂. The emission of carbon monoxide, hydrocarbon, nitrogen oxides and smoke are averagely decreased by 27%, 27%, 5%, and 52%, respectively under speed characteristic at full load [27]. This study [27] tacitly suggests that biodiesel from soybean crude oil can be used as a substitute for diesel in diesel engine.

However, several numbers of researchers reported slight increase of NO_x emissions for biodiesel [26,27,31,33,91,106,107]. According to Haas et al. [107] compared with petroleum diesel fuel, emissions of total hydrocarbons, particulates, and carbon monoxide were reduced 55%, 53%, and 48%, respectively, with neat soapstock biodiesel. Total nitrogen oxides increased 9%. Operation on a 20 vol.% blend of soapstock biodiesel in petroleum diesel gave reductions of hydrocarbons, particulate matter, and carbon monoxide by 27.7%, 19.7%, and 2.4%, respectively, relative to petroleum diesel. Nitrogen oxide emissions increased 1.3%. It is quite obvious that with biodiesel, due to improved combustion, the temperature in the combustion chamber can be expected to be higher and higher amount of oxygen is also present which leads to formation of higher quantity of NO_x in biodiesel-fueled engines. The most commonly accepted justification for this behaviour lies in the higher cetane number of the biodiesel that reduces the ignition delay. Reduction of ignition delay can increase NO_x emissions [109]. This is in good agreement with the results obtained by Lance et al. [110]. However, higher oxygen content also leads to lower calorific values, which may result in significant power losses and the increase of specific fuel consumption. The increased fuel consumption with biodiesel resulted in increased H₂O and CO₂ in the engine exhaust gas. For example, the CO₂ contents of the engine exhaust gas from the combustion of B0 (diesel), B20, B50 and B100 (RME) were 4.86%, 4.90%, 5.00% and 5.10%, respectively, for engine condition 1 (IMEP ¹/₄4.5 bar) and increased to 6.60%, 6.90%, 7.00% and 6.90%, respectively, for engine condition 2 (IMEP 1/46.1 bar) [111].

Oxygen content and cetane number can also be varied based on biodiesel feedstock and therefore the emission characteristics are different for different biodiesel. Lance et al. [110] investigated the exhaust emissions for B20 blends from different FAME sources; namely coconut, jatropha and rape methyl esters and the European Regular Diesel which was used as the base for all blends. The premium fuel and B20 HVO (hydrogenated vegetable oil) were also included for comparison. They showed that at equivalent blend level of B20, RME tended to give amongst the highest HC, CO and NO_x emissions compared to JME or CME (Fig. 3). They also added that B20 RME had 30% higher NO_x emissions as compared to that of diesel.

With regard to the selection of the biodiesel fuels, most of the proposals agree to select more saturated biodiesel fuels in order to reduce NO_x emissions. Chapman et al. [112] proposed to blend soybean-oil biodiesel with short-chain methyl esters such as caprilic (C8:0) or capric (C10:0) ones, in a proportion of 15% of short-chain esters. The short chain was required to avoid worsening the cold flow properties. They measured 2.8% decreases in NO_x emissions with 20% blends of biodiesel including short-chain esters as compared to those with 20% blends of unmodified biodiesel. They

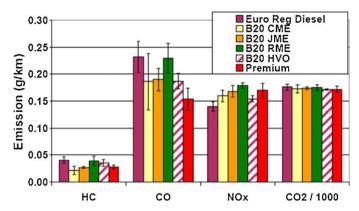


Fig. 3. Emissions effects of FAMEs and HVO (hydrogenated vegetable oil) at B20 level [110].

also achieved 1.5% reductions by hydrogenating the soybean-oil biodiesel. In a later work [113] these authors also hydrogenated the original soybean-oil prior to transesterification. They obtained iodine numbers of 90 by turning linoleic (C18:2) and linolenic (C18:3) acids into oleic acid (C18:1). They measured reductions in NO $_{\rm X}$ emissions mainly at low engine speed. Knothe et al. [114] compared conventional diesel fuel with oleic methyl ester (C18:1), palmitic methyl ester (C16:0) and lauric methyl ester (C12:0) in a six cylinder engine under transient conditions, and observed a 4% and 5% reduction in NO $_{\rm X}$ emissions for the saturated palmitic and lauric esters, respectively, whereas a 6% increase for the oleic ester

During high temperature application, biodiesel can easily be oxidized and thereby can also influence the performance and emission as well. Monyem and Van Gerpen [76], found that the oxidized biodiesel can reduce the exhaust emission significantly while the engine performance for both oxidized and unoxidized biodiesel is almost similar. They also observed that oxidized biodiesel had about 15% less CO emissions than the unoxidized biodiesel and 28% less than No. 2 diesel fuel. Oxidized biodiesel also reduced the HC emissions by 21% and 54% compared to the unoxidized biodiesel and No. 2 diesel, respectively. The neat oxidized biodiesel had about 13% higher NOx emissions than the No. 2 diesel fuel while the unoxidized biodiesel had about 14% higher. They explained that the increased cetane number of oxidized biodiesel from 51.1 (unoxidized) to 72.7 (oxidized) could be attributed to minimize the emission significantly. In a recent study, slightly different behaviour of oxidation was observed by Ryu [34], where he has stated that use of antioxidant can minimize the BSFC by reducing oxidation. He also added that the efficiency of antioxidants in reducing BSFC is in the order TBHQ > PrG > BHA > BHT > α -tocopherol. Hess et al. [115] also reported that the addition of butylated hydroxyanisole (BHA) or butylated hydroxytoluene (BHT) in biodiesel reduced NO_x emissions. Lin et al. [85] proposed to use water-biodiesel emulsions to reduce NO_x emissions although they did not provide experimental confirmation. Upon increasing the air inlet temperature, rapeseed oil methyl ester and diesel blend was found to reduce carbon monoxide, NO_x and smoke emissions considerably [116]. However, compared with the diesel fuel, NO_x emission with biodiesel was largely reduced when EGR (Exhaust Gas Recirculation) was applied [117]. Cheng et al. [35] observed that 10% methanol (BM10) and 10% fumigated methanol (air/methanol) can reduce NO_x by 6.2% and 8.2%, respectively. In conclusion, it is seen that emission in biodiesel fuelled engine can be further minimized by adding additives, methanol or fumigated methanol, by increasing air inlet temperature as well as by using EGR (Exhaust Gas Recirculation).

5. Engine durability

In order to assess the raised problems due to use of biodiesel, a number of long term durability tests have been conducted with B20 as well as higher percentage of blends. Several of these studies have been conducted by some researchers in National Renewable Energy Laboratory, sponsored by U.S. Department of Energy and two of the most significant are reviewed here. Kenneth et al. [48] operated nine identical 40 ft transit buses on B20 and diesel for a period of two years - five of the buses operated exclusively on B20 and the other four on petroleum diesel. They have shown 1.2% lower fuel economies for B20 and this is expected due to lower energy content of B20 as compared to diesel fuel. Their oil analysis results indicate no additional metal wear for B20, rather soot levels in the lubricant were significantly lower for B20 vehicles. But, fuel filter plugging was the major problem for B20 buses which was seemed to cause by the presence of high levels of plant sterols in the biodiesel or other fuel quality issues. In conclusion, they have shown engine and fuel system related maintenance costs were nearly identical for both diesel and biodiesel blend groups until the final month of the study. But component replacements like injector and cylinder head near the end of the study on one B20 bus caused average maintenance costs to be higher for the B20 group (\$0.07 vs. \$0.05 per mile). Another experiment conducted by Fraer et al. [62] on four 1993 Ford cargo vans and four 1996 Mack tractors (two of each running on B20 and two on diesel) for 4 yr in order to investigate the durability of engine parts. No differences in wear or other issues were noted during the engine teardown. However, the Mack tractors operated on B20 exhibited higher frequency of fuel filter and injector nozzle replacement. Biological contaminants may have caused the filter plugging. A sludge buildup was noted around the rocker assemblies in the Mack B20 engines. The sludge contained high levels of sodium, possibly caused by accumulation of soaps in the engine oil from out-of-specification biodiesel.

National Biodiesel Board (NBB) [47] performed durability test for 1000 h duration on 1987 Cummins NI4 engine by B20 (soybean methyl ester). Though this test was intended to be of 1000 h duration, it had to be terminated at 650 h due to failure of the engine pump, a part of the fuel system. This failure was caused by build up in the pump of a residue composed of fatty acid esters, free fatty acids, and acid salts. The same residue had plugged a fuel filter and the pump earlier in the durability test. Fuel injectors were in good condition at the end of the test. Oil analysis revealed no significant degradation. It was proposed that the operational problems experienced during this test were caused by instability toward oxidation of the B20 fuel. NBB [46] carried out another 1000 h durability test using a DDC 6V-92TA, electronic controlled engine with B20 methyl soyester blend. At about 700 h, they have observed significant deposits on air box covers, piston components and injectors. The fuel lines, fuel filters, and fuel transfer pump were needed to replace during this brief shut-down at 700 h. At the end of final 250 h, the engine was dissembled and substantial deposits were found on many engine components. The source of these deposits appeared to be the lube oil. Cavitation erosion of the injector needle valves had caused injectors to deteriorate to the point that almost no fuel atomization was occurring. Deteriorating fuel pump seals were proposed to have introduced microscopic air bubbles into the fuel causing the cavitation erosion. Elevated soot, wear metals in the lubricant, softening of fuel system seals were observed. Broken fire and compression rings were also found on several cylinders.

Some truckers have also complained that fuel filter clogging is increasing as animal fat and soybean-based fuels are being introduced nationwide [118]. Fuel system problems, including filter plugging have been documented in the United States, along with fuel filter plugging in vehicles that use B100 or biodiesel blends. According to a survey conducted by the Minnesota Trucking Associ-

ation, 62% of 90 fleets said they had experienced fuel filter plugging [119]. Humberg et al. [120] surveyed the experience of state transportation agencies with B20 and petroleum diesel. Almost half of the states using B20 reported more fuel filter plugging issues with B20 than with petroleum diesel. Small declines in fuel economy with B20 were observed. No noticeable changes in fuel pump and fuel injector durability or unusual impacts on engine oil analyses were reported.

According to Peckham [121], fuel filter plugging and engine deposit formation may be related to the formation of total insolubles, but B100 does not produce significant insolubles when tested by storage stability tests. This may be due to the solubility of the polar degradation by-products in the somewhat polar biodiesel, but these by-products can then become insoluble when the biodiesel is blended into the non-polar diesel fuels. Oxidation and polymerization of biodiesel have also been recognized as causes of filter plugging, fuel injector deposits, injector coking and corrosion [18,122]. The solvent like properties of biodiesel also dissolve elastomers as well as fuel tank deposits and lead to fuel filter and injector plugging as a consequence of increased viscosity [123–125].

Filter plugging problem in biodiesel-fueled engine becomes more severe in cold weather [126,127]. At low temperatures, wax crystals begin to form in diesel fuel and with further decreasing in temperature, the wax crystals will increase and can ultimately clog fuel filters and injectors and will finally gel and cease flowing. Similar issues also affect biodiesel, but at relatively higher temperatures. The temperature at which diesel fuel begins to crystallize is called the cloud point [128]. According to Benjumea et al. [129] petroleum diesel has a cloud point of around -5 °C whereas B20 and B100 (palm oil based) have cloud points of about 0 and 18 °C, respectively. A fuel may still work in an engine even if the temperature is below the cloud point. However, the fuel will definitely not work below the pour point (after it has gelled). Silva et al. [130] observed that addition of 5 vol.% of the butanal/glycerol acetal reduced the pour point of animal fat biodiesel (methyl ester) from 18 to 13 °C. Addition of ethanol in biodiesel was also found to improve the cold flow properties [131]. According to Lin and Li [95], highly unsaturated fatty acids (HUFA) are effective in improving low-temperature fluidity. In addition, fuel additives can also be used in petroleum diesel and biodiesel to lower cloud points and help alleviate the associate problems.

6. Conclusions

The following conclusions can be drawn from this study:

- 1. In laboratory investigation, biodiesel from different origins is always seen to provide better lubricity than that of diesel fuel. However, in long term test it loses its lubricity due to its corrosive and oxidative nature.
- Auto-oxidation, hygroscopic nature, higher electrical conductivity, polarity and solvency properties of biodiesel cause enhanced corrosion of metals and degradation of elastomers. In addition, presence of free fatty acid, degree of unsaturation, impurities remaining after processing can also increase corrosion of automotive materials. In turn, upon exposure to metals, fuel properties of biodiesel can also be changed.
- 3. Biodiesel can improve combustion and hence has higher brake thermal efficiency than petroleum diesel. Engine power is reduced slightly or not at all because the consumption of biodiesel increases enough in order to compensate its lower heating value. However, overall biodiesel permits acceptable engine performance and it could be further improved if viscosity could be reduced.

- 4. Higher concentration of oxygen in biodiesel improves lubricity, combustion and reduces emissions while it slightly increases NO_x. Addition of alcohol (methanol/ethanol) can further reduce the emissions and can decrease viscosity. But both alcohol (methanol/ethanol) and oxygen can enhance the corrosion of automotive materials. However, different types of additives (e.g. TBHQ, PrG BHA, BHT) can be used to improve lubricity, corrosion resistance as well as engine performance and emissions.
- 5. During durability test, the common problems identified by the researchers are failure of fuel pump, filter plugging, injector coking, moving parts sticking etc.
- 6. The area of concern to use biodiesel successfully includes viscosity, flow properties, oxidative stability, solvency, corrosion, free methanol, esterification by-products, formation of sediments, gels or salts, microbial growth etc. Although the effect of these factors on applicability of biodiesel has closely been examined, the successful techniques to overcome these problems have hardly been investigated in details. The technical advantages of biodiesel over petroleum diesel fuel include high cetane number, higher flash point, oxygen content and sulphur-free, improved lubricity, reduced emissions etc.

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